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Prediction of β-glucosidase and β-glucosaminidase activities, soil organic C, and amino sugar N in a diverse population of soils using near infrared reflectance spectroscopy

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ABSTRACT

There is a need for methods that can rapidly measure multiple biological properties simultaneously. A near infrared spectroscopy (NIRS) method was used to predict β-glucosidase (EC 3.2.1.21) and β-glucosaminidase (NAGase, EC 3.2.1.52) activities, and soil organic C and amino sugar N concentrations in 184 diverse soils of Ohio. The laboratory-measured values of the variables were calibrated against NIR spectral data with partial least squares regression analysis. Statistical analysis of the spectral data was done using the multivariate analysis software Unscrambler 8.0 (CAMO Inc). The first differential transformation of the spectral data in the NIR region (1100–2498 nm) generally yielded best results for developing multivariate calibration models. The multivariate models developed were validated using the full cross validation method and the test set method with a test set size of approximately 45 samples. The R^2 values, testing variation between concentrations as measured by the NIR method and chemical methods, were 0.91 for organic carbon (OC), 0.92 for amino sugar N, and 0.82 for both soil β-glucosidase and β-glucosaminidase enzyme activities. Our study showed that the NIRS method has the potential to simultaneously, rapidly and accurately predict values of multiple related variables. The equipment needed for the NIRS method is not expensive and can be used where very large numbers of samples need to be rapidly analyzed. Indeed, the prediction equations can be constantly improved as more data points are entered into the correlations between laboratory-measured values and NIRS values.

1. Introduction

The measurement of soil properties often requires a separate standard methodology for each individual property. This can be tedious and costly, especially if large numbers of samples are to be analyzed. As an alternative to standard methodologies, the near infrared reflectance spectroscopy (NIRS) approach provides the opportunity for rapid, concurrent, and inexpensive analysis (Ben-Dor and Banin, 1995; Chang et al., 2001). The process is non-destructive and requires a minimal amount of sample (Chang et al., 2001). Extensive sample preparation is typically unnecessary, which eliminates chemical waste and conserves time (Rinnan and Rinnan, 2007). Because large numbers of samples can be analyzed quickly, statistical confidence in the calculations can easily be improved upon (Janik et al., 1998).

To detect the presence of analytes, NIRS measures the diffuse reflectance of electromagnetic radiation created by the vibrational modes of molecular bonds (Ben-Dor and Banin, 1995; Rinnan and Rinnan, 2007). Physical characteristics, such as particle size and arrangement, also affect NIR spectra. To quantify the raw spectral data, multivariate calibration is used to establish a linear relationship between absorption calculations [A (absorbance) = log (1/R) (reflectance)] and analyte concentration (Ben-Dor and Banin, 1995; Chang et al., 2001). If an analyte does not absorb light in the NIR range, correlating properties can be measured instead (Terhoeven-Urselmans et al., 2006).

Popular NIRS calibration methods for soil property analysis include Fourier regression, partial least square regression (PLSR), neural networks, principal component regression (PCR), stepwise multiple linear regression (SMLR) and locally weighted regression (LWR) (Chang et al., 2001). To select and verify the calibration model, a validation process is employed that compares the concentration predicted from the calibration equation with sample concentrations measured using a standard analytical technique (Ben-Dor and Banin, 1995) for a subset of the samples. The degree of correlation between measured and predicted results (R^2) and the ratio between measurement error and prediction error (RPD) are commonly used

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to assess the accuracy of the NIRS model (Ben-Dor and Banin, 1995; Cohen et al., 2005).

Both soil organic C and amino sugar N are fractions of soil organic matter and major sources of nutrients for plants and soil organisms (Bauer, 1994). Soil organic C fuels the metabolic activity of microorganisms (Bauer, 1994) and is often considered an important indicator of soil productivity (Reeves, 1997; Shukla et al., 2006). β-glucosidase, which releases glucose, also helps provide energy to soil microorganisms and is directly related to soil organic C content (Eivazi and Tabatabai, 1988; Bandick and Dick, 1999). This enzyme's activity has been used to closely monitor rapid changes in soil organic C brought about by soil management effects (Bandick and Dick, 1999).

Despite such advantages, the use of enzyme activities to indicate soil quality or to study soil functions is often restricted to biochemical or microbiological laboratories. However, basic soil properties such as mineral content, total organic C and N, pH, C and N mineralization, biomass C, soil respiration and moisture content have been successfully determined by spectral methods (Chang et al., 2001; Cohen et al., 2005). For example, NIRS models have been tested and developed for addressing regional soil performance issues or "specific soil queries." The NIRS method was used to explore the effects of a wildfire and earthworm activity on soil ecosystem functions (Cécillon et al., 2009; Cassagne et al., 2008) and for the determination of Florida wetland soil quality (Cohen et al., 2005). Moros et al. (2009) created NIRS models to determine toxic metal concentration, lime content, organic matter and electrical conductivity for soils in the Murcia region of Spain. NIRS has also been used to rapidly determine activities for the soil enzymes β-glucosidase, acid and alkaline phosphatases, arylsulfatase, dehydrogenase, peptidase, and urease (Cohen et al., 2005; Mimmo et al., 2002; Reeves et al., 2000; Zornoza et al., 2008).

The measurement of mineralizable soil N is crucial for determining the needed amounts of fertilizer, but a standardized predictive measurement procedure has been difficult to establish. Chemical indicators, such as NO_3^-, often yield inaccurate results (Mulvaney et al., 2001). The NIRS method could improve the feasibility of using biological indicators, such as β-glucosaminidase activity, for rapidly estimating N mineralization. Amino sugar N analysis has emerged as a potentially improved procedure for gauging mineralizable soil N content (Mulvaney et al., 2001). The activity in soil of β-glucosaminidase, which produces amino sugars, has also been associated with the N acquisition process of microorganisms (Parham and Deng, 2000; Sinsabaugh and Moorhead, 1995). In reality, a suite of biological C and N indicators may be much more accurate in assessing N mineralization in soil, and thus native soil N fertility, than a single soil parameter.

There is, thus, a need for methods that can rapidly measure multiple biological properties simultaneously. Measurement of multiple soil properties at one time is clearly feasible using the NIRS method. Our research objective, therefore, was to develop and test a NIRS model for the prediction of organic C content, amino sugar N concentration, and the activity of the soil enzymes β-glucosidase and β-glucosaminidase, in a set of diverse Ohio soils.

2. Materials and methods

2.1. Soil sample collection and storage

The majority of the soil samples used in the development of the NIRS calibration model were chosen at random from the Soil Testing Laboratory at the Ohio Agricultural Research and Development Center (Wooster, OH). The exact origins of sites in Ohio were not known for 169 of the total 184 samples. The total amount of samples (184) collected exceeded the recommended minimum (150) of soil samples that are needed to develop NIRS predictive equations (Windham et al., 1989). Collected samples were air-dried and sieved through a 2 mm mesh screen. Soil samples were stored for several weeks to several months in cardboard boxes at room temperature.

2.2. Standard soil property methodologies

The organic C content was determined in the STAR Laboratory at the Ohio State University, Wooster, OH (http://oardc.osu.edu/starlab/) by correlating loss-on-ignition values (Storer, 1984) with organic C values (International Organization for Standardization, 1995) using a regression equation ($R^2 = 0.9929$) developed after analyzing a very large number of samples in the STAR Laboratory. The amino sugar N concentration, a fraction of total organic C and N, was estimated using the Illinois Nitrogen Soil Test by incubating samples at 55 °C for 5 h in 2 M NaOH as described by Khan et al. (2001). Spectrophotometric assays were used to measure the activity of β-glucosidase (Eivazi and Tabatabai, 1988) by incubating 1 g soil (air-dry basis) for 1 h with p-nitrophenyl-β-D-glucoside (Sigma Chemical Co., St. Louis, MO, USA) at pH 6.0 (modified universal buffer). β-glucosaminidase (Parham and Deng, 2000) was measured by incubating 1 g soil for 1 h with *p*-nitrophenyl-*N*-acetyl-β-D-glucosaminidine (Sigma Chemical Co.) at pH 5.5 (acetate buffer).

The properties measured, along with the references for the methods used to measure these properties, are listed in Table 1. Statistical correlations were performed to determine inter-variable relationships between these soil properties.

2.3. Spectral analysis of the soil samples

A FOSS-TECATOR 6500 spectrometer was used to collect spectral data for the soil samples. Prior to analysis, samples were oven-dried (60 °C) for twelve hours and stored in a dessicator. Using a rotating cup with a quartz lens, reflectance measurements were taken from 400 to 2498 nm that covered both the visible and near infrared regions of electromagnetic radiation. Data were collected every 8 nm at a resolution of 2 nm resulting in 1050 data points for each sample. Prior to preprocessing, the reflectance data was converted to units of log (1/R) and the measured soil property data were entered into a spreadsheet as *X*-values and *Y*-values, respectively.

Unscrambler version 8.0 (CAMO Inc., 2003) software was used to process the spectral data. Two data sets were created using 700 data points from the 1100–2498 nm NIR wavelength region and 1050 data points from the 400–2498 nm visible-NIR wavelength region. The 400–2498 nm, or extended, data set was reduced by averaging every four adjacent spectral data points to produce 263 new data points. Similarly, the 1100–2498 nm data set was reduced to 175 data points from 700 spectral data points.

Table 1
Soil C enzymes and properties measured in 184 soil samples (air-dried).

Carbon enzymes and properties[a]	Mean	SD	Range	Method reference
Soil organic C (g kg^{-1} soil)	24.1	18.0	1.1–127	Storer, 1984
Amino sugar N (mg kg^{-1} soil)	216	96.9	9.04–614	Khan et al., 2001
β-glucosidase (mg kg^{-1} soil h^{-1})	87.5	62.7	0.27–328	Eivazi and Tabatabai, 1988
β-glucosaminidase (mg kg^{-1} soil h^{-1})	34.4	25.2	0.28–116	Parham and Deng, 2000

[a] For each C enzyme or property measured, the number of samples (n) in the data set is 184. SD = Standard deviation.